



Figure 1. Polarograms

- A. Phthalic anhydride
B. Mixture of phthalic anhydride and maleic anhydride

polarographic wave of a solution of 0.01280 mole per liter of phthalic anhydride. Curve B is the wave of the same solution of phthalic anhydride to which maleic anhydride was added. The wave height, h_1 , of the 0.01280 *M* phthalic anhydride, when present alone in the electrolytic solution, is equal to h_2 , the wave height of phthalic anhydride in the presence of 0.01647 *M* maleic anhydride. This suggested the possibility of determining these two anhydrides when present together in mixtures. Curiously enough, mixtures of the two anhydrides do not produce the maximum obtained from solutions containing only one (Figure 1).

To test the possibility of analyzing a mixture of anhydrides having distinctly different half-wave potentials, a solution (0.3 *M* lithium chloride, 50-50 benzene-methanol) containing weighed amounts of both phthalic and maleic anhydrides was prepared. The polarogram obtained with this solution resembled curve B,

Table III. Analyses of Solutions of Anhydride Mixtures

Anhydride Mixture	Amounts (Grams/40 Ml.)		Relative Error, %
	Added	Found	
Solution 1 phthalic maleic	0.0451	0.0443	-1.8
	0.0451	0.0472	+4.7
Solution 2 phthalic maleic	0.0335	0.0356	+6.3
	0.0953	0.0938	-1.5
Solution 3 phthalic maleic	0.0525	0.0496	-5.5
	0.0677	0.0689	+1.8
			Av. ± 3.6

Figure 1, in having two distinct waves, one at -0.75 volt due to the maleic anhydride and the other at -1.16 volts due to the phthalic anhydride. From the proportional increases in the respective wave heights caused by adding weighed increments of phthalic and maleic anhydride, the quantities of phthalic and maleic anhydrides originally present in the mixture were calculated. Table III shows the results obtained using three solutions of mixtures of varying amounts of phthalic and maleic anhydride. These data show that it is possible to estimate the amounts of each of these anhydrides, when present together, with a relative percentage error of $\pm 4\%$.

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LITERATURE CITED

- (1) Kappelmeier, C. P. A., and van Goor, W. R., *Anal. Chim. Acta*, **2**, 146-9 (1948).
- (2) Lewis, W. R., and Quackenbush, F. W., *J. Am. Oil Chemists Soc.*, **26**, 53-7 (1949).
- (3) Lingane, J. J., and Laitinen, H. A., *IND. ENG. CHEM., ANAL. ED.*, **11**, 504-5 (1939).
- (4) Willits, C. O., Ricciuti, C., Knight, H. B., and Swern, D., *ANAL. CHEM.*, **24**, 785 (1952).

Polarographic Studies of Oxygen-Containing Compounds

Acid Anhydrides

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CONTINUED study of the polarographic behavior of oxygen-containing functional groups in nonaqueous, lithium chloride electrolytic solution (4) has shown that α,β -unsaturated organic acid anhydrides are polarographically reducible. The polarographic reduction of acid anhydrides produces wave heights which have a linear relationship to concentration. This suggested that the polarographic method would provide a direct means for their determination.

APPARATUS

A Sargent Model XXI polarograph was used to obtain the current-voltage curves. The sensitivity settings of this instrument were calibrated against known resistances. The capillary m and t values were 3.59 mg. per second and per 1.35 seconds, respectively, which gave a capillary constant, $m^2/t^{1/2}$, of 2.46 $\text{mg.}^2/\text{sec.}^{-1/2}$. The m and t values were obtained using an open circuit with the polarographic cell maintained at $25^\circ \pm 0.1^\circ \text{C}$. and with the capillary immersed in the nonaqueous electrolytic solution.

The electrolytic cell is that described by Lingane (3) and modified by Willits *et al.* (4).

MATERIALS

The electrolytic solution described by Lewis and Quackenbush (2), which consisted of 0.3 *M* lithium chloride in equal volumes of absolute methanol and benzene, was used in these studies.

ANHYDRIDES (Eastman Kodak, White Label grade, except as indicated).

Benzoic anhydride. Melting point, 42° to 3°C ., 97.0% pure [determined by the "anilic acid number" method (1)].

n-Butyric anhydride, 93.8% pure (1).

n-Butyl ester of aconitic anhydride prepared in this laboratory, 97.0% pure (determined by hydrolysis and acidimetry).

Caproic anhydride.

Citraconic anhydride, 100.0% pure (1).

Crotonic anhydride, 98.6% pure (1).

Maleic anhydride, 98.8% pure (1).

Phthalic anhydride, purest commercial material, 99.8% pure (1).

Succinic anhydride.

ACIDS. Aconitic acid, American Sugar Refining Co.

Benzoic acid, prepared in the authors' laboratory, melting point 122°C .

Crotonic acid, Eimer and Amend, reagent grade.

Maleic acid, Eastman Kodak, White Label grade.

Polarographic studies of acid anhydrides were undertaken to determine whether their polarographic characteristics in nonaqueous system could be used for their identification and determination. α,β -Unsaturated anhydrides were found to be polarographically reducible and the corresponding acids and esters, with the exception of maleic acid, did not interfere with the polarographic waves of the anhydrides. Saturated acid anhydrides did not show polarographic reduction. α,β -Unsaturated acid anhydrides can be identified in the presence of saturated anhydrides and can be determined if the identity of the unsaturated anhydride is known. It is also possible to determine the composition of a mixture of two unsaturated anhydrides if their identity is known, and if their half-wave potentials are sufficiently widely separated.

Phthalic acid, prepared from pure phthalic anhydride by boiling with water for several minutes followed by cooling to precipitate the acid.

ESTERS. Dimethyl phthalate, Eastman Kodak, White Label grade.

Di-2-ethyl hexyl maleate, Carbide and Carbon Chemicals Corp.

Methyl benzoate, Eastman Kodak, White Label grade.

Methyl crotonate, Eastman Kodak, White Label grade.

Monocyclohexyl phthalate, Barrett Division of Allied Chemical & Dye Corp.

Monomethyl phthalate, prepared by refluxing phthalic anhydride with methanol for 30 minutes and crystallizing from water.

PROCEDURE

A weighed sample was dissolved in a measured volume of the lithium chloride, methanol-benzene, electrolytic solution and the polarographic waves were obtained as described previously (4). All half-wave potential measurements were made against the saturated calomel electrode as reference electrode and all half-wave potentials were corrected for IR drop.

Concentrations of anhydrides of less than 0.00040 mole per liter showed no tendency to form maxima whereas with higher concentrations, sharp maxima were formed. The usual maximum suppressors such as methyl red and gelatin had no effect on these maxima. Materials with high viscosities such as the polyacrylates and glycerin were also tried as suppressors but without success. Although abnormally high maxima were obtained with higher concentrations, the wave heights were reproducible when measured at the minimum point following the maximum, and these wave heights were directly proportional to the concentration of the anhydride. The linearity of the wave heights vs. concentration was determined from the four to six polarograms obtained for a number of the compounds. Each polarogram was obtained from individually weighed samples.

To determine if there was any interaction between the acid anhydrides and the electrolytic solution, the anhydrides were added in increments to the solution with extended intervals between additions (over one half hour). It was observed that the successive wave heights were directly proportional to the amount of anhydride added. Had there been any reaction between the anhydrides and the solvent, this proportionality would not have existed.

DISCUSSION OF RESULTS

Of the nine anhydrides listed above only the six with α,β -unsaturated linkages were reducible in the nonaqueous electrolytic solution used (0 to -2 volts). A similar observation had been made in a previous study (4) when only α,β -unsaturated aldehydes and ketones were found to be reducible under these conditions. None of the saturated anhydrides was reduced, indicating that under the conditions used unsaturation is required for reduction and that polarographic determination of α,β -unsaturated anhydrides in the presence of saturated anhydrides is possible. Table I shows the polarographic characteristics of the six unsaturated acid anhydrides. It is apparent from the table that the diffusion current constants are independent of concentration in the ranges studied.

A number of acids and esters corresponding to the reducible anhydrides were studied to determine whether they were also reducible and, if so, whether their half-waves were sufficiently different from that of the anhydride not to interfere with the an-

alysis of mixtures. Table II shows the polarographic behavior of five of the reducible anhydrides and eleven acids and esters derivable from them. The table shows that, with the exception of maleic acid, the acids or esters either are nonreducible or produce noninterfering polarographic waves. It should thus be possible to determine benzoic, crotonic, phthalic, and aconitic anhydride in the presence of their corresponding acids or esters. In the case of maleic anhydride, however, the first wave of maleic acid ($E_{1/2} = -0.84$ volt), would interfere with the wave of maleic anhydride ($E_{1/2} = -0.72$ volt).

It is not possible to distinguish between the acid anhydrides in a mixture of two or more when their half-wave potentials are too close to one another to permit differentiation of the separate waves. For example, the maleic anhydride wave, having a half-wave potential of -0.72 volt, cannot be distinguished from that of butyl ethoxy ester of aconitic acid anhydride ($E_{1/2} = -0.77$ volt) when these anhydrides are present together. However, the $E_{1/2}$ of the maleic anhydride wave is sufficiently distant from that of phthalic anhydride ($E_{1/2} = -1.12$ volts) to permit their quantitative estimation when they are present together. Figure 1 shows a typical analysis of such a mixture. Curve A is th

Table I. Polarographic Characteristics of Reducible Acid Anhydrides

Acid Anhydride	No. of Tests	Concn. Range, Millimoles/Liter	Half-Wave Potential ^a	$\frac{id}{Cm^{2/3}t^{1/2}}$
Maleic	4	22.5-51.7	-0.72 ± 0.02	2.14 ± 0.03
Aconitic (butyl ester)	5	4.7-16.7	-0.77 ± 0.02	1.27 ± 0.03
Citraconic	5	6.5-63.1	-0.84 ± 0.04	1.76 ± 0.08
Phthalic	5	7.4-21.4	-1.12 ± 0.00	2.54 ± 0.03
Benzoic	6	8.8-16.2	-1.62 ± 0.02	3.08 ± 0.12
Crotonic	5	3.5-21.6	-1.62 ± 0.03	3.33 ± 0.06

^a Corrected for IR drop.

Table II. Comparison of Polarographic Characteristics of Acid Anhydrides, Acids, and Esters

Compound	Half-Wave Potential	$\frac{id}{Cm^{2/3}t^{1/2}}$
Benzoic anhydride	-1.62	3.08
Benzoic acid	None ^a	None
Methyl benzoate	None	None
Crotonic anhydride	-1.62	3.33
Crotonic acid	None	None
Methyl crotonate	None	None
Phthalic anhydride	-1.12	2.54
Phthalic acid	None	None
Mono-methyl phthalate	-1.48	2.02
Dimethyl phthalate	None	None
Mono-cyclohexyl phthalate	-1.56	1.86
Maleic anhydride	-0.72	2.14
Maleic acid	-1.38 (poorly defined)	0.59
	-0.84	1.33
Di-2-ethyl hexyl maleate	-1.33 (poorly defined)	2.22
	-1.30	3.15
Butyl ester of aconitic acid	-0.77	1.27
Aconitic acid	-1.24	2.84

^a No reduction wave from 0.0 to -2.0 volts in the electrolytic solution used.